

CALIBRATION OF NAPL FIELD SCREENING METHODOLOGIES FOR INCLUSION IN A COMPREHENSIVE NAPL INVESTIGATION AT A SUPERFUND SITE IN NEW JERSEY

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Abstract

The use of mathematical methods for assessing a site for the potential presence and distribution of NAPLs is gaining widespread acceptance by industry and regulators alike. An example is the method developed by Feenstra, et al. (1991) for evaluating soil quality data. However, the use of such mathematical methods for NAPL delineation requires the acquisition of analytical data, which can be cost prohibitive at large, complex sites where multiple potential NAPL impacted areas exist. This paper describes and discusses the process employed at one such site to calibrate NAPL field screening methods to site conditions in order to facilitate reliance upon routine field screening methods to assess soil samples for the presence or absence of NAPL. The NAPL field screening methodologies employed were 1) visual inspection, 2) field head-space measurement, 3) hydrophobic dye shake test, and 4) ultraviolet fluorescence. The calibration process consisted of two components. The first component of the process was bench-scale studies to evaluate the applicability of the field screening methods to specific organic compounds routinely detected at the site and considered likely NAPL constituents. The second component of the process was the actual calibration of the NAPL field screening methods to typical soils encountered at the site. This component included comparing the results of the NAPL field screening to those derived mathematically for two potential NAPL impacted areas at the site. A total of 77 soil samples were collected from these two areas that were subjected to both the NAPL field screening methodologies and mathematical methods. The NAPL field screening methodology calibration process determined the applicability, and established the limitations, of the field screening methods for this site. As a result, a comprehensive NAPL field investigation program was developed for the site in which the calibrated NAPL field screening methodologies were the primary tool for delineating the NAPL impacted areas, with only periodic analytical samples required for confirmation and as a calibration check. The program afforded a streamlined, cost-effective investigation which was approved by the United States Environmental Protection Agency (USEPA).

Introduction

Non-aqueous phase liquids (NAPLs) are widely recognized by both industry and regulators as one of the most significant issues to be addressed when investigating hazardous waste sites. Not only do NAPLs persist in soils, serving as a potential exposure risk, but they can also serve as a long-term source for ground water contamination. As long as significant quantities of residual NAPLs are present and contributing to a dissolved-phase ground water contaminant plume, even the most well-designed ground water remediation system cannot be expected to "cleanup" the entire plume in a reasonable time frame. With the overall remedial objective at many sites being "aquifer restoration", the presence of NAPLs can

present a difficult dilemma to overcome. Therefore, determining whether or not NAPLs are present at a site, and their spatial distribution, is essential in evaluating potential remedial or containment technologies.

This article presents a case study where NAPL field screening methods were calibrated to site-specific conditions for routine use as the primary mechanism for determining the likely presence or absence of residual NAPLs in a soil sample. The four NAPL field screening methods employed were: visual inspection; field head-space measurement; hydrophobic dye shake test; and ultraviolet fluorescence. The NAPL field screening calibration process consisted of the following three components:

1. Development of an Operational Definition of NAPL (ODN) for determining the likely presence or absence of residual NAPL in a soil sample.
2. Performance of bench-scale studies to determine the applicability and general sensitivity of the NAPL field screening methods to the type of NAPLs and soil characteristics at the site.
3. Field calibration of the NAPL field screening methods using site soil samples from two potential NAPL source areas where the probability of residual NAPLs being present was high.

The calibrated NAPL field screening methods were then incorporated into a comprehensive NAPL field investigation at the site as the primary mechanism for determining the presence or absence of NAPL in soil samples. The field investigation was the second of two components of a "NAPL Action Plan" developed for the site, as required by the United States Environmental Protection Agency (USEPA) in the Consent Decree administered to the site owner. The initial component utilized an integrated approach to evaluate existing data from the site with regards to the presence or absence of NAPLs (Watkins, Sieber, and Christians, 1995).

The initial component of the NAPL Action Plan identified those potential NAPL source areas at the site which warranted further investigation and NAPL delineation. The overall objective of the NAPL field investigation was to define, to the extent possible, the three-dimensional envelope within which any NAPLs were contained. The routine use of calibrated NAPL field screening methods would be a cost-effective approach toward meeting this overall objective. The true cost savings would be realized by reducing dependence on analytical sample results to determine the presence or absence of residual NAPLs in soil samples. Another advantage of using the calibrated field screening methods is that they could be routinely applied to every sample collected in the field, affording better coverage and expedient turnaround time on results.

The study site is a Superfund site in New Jersey underlain by the Cohansey Sand of the New Jersey Coastal Plain. The site is situated on approximately 1,400 acres, with the former manufacturing facilities occupying approximately 300 acres of the total. The undeveloped portion of the site is wooded, consistent with the pine barrens character of the region. The site is bounded on the east and northeast by the Toms River, while the remainder of site is bounded by residential and light commercial areas. The layout of the site is illustrated on Figure 1, as well as the primary potential NAPL source areas.

This article focuses on the process that resulted in the development of calibrated NAPL field screening methods for use at the study site. As such, it is well beyond the scope of this article to provide great detail regarding each component of the process. However, sufficient detail is provided to validate, and provide an overall understanding of, the process.

Geologic Setting

The study site is situated within the Atlantic Coastal Plain physiographic province and is underlain by a complex stratigraphic sequence of largely unconsolidated sands, silts, and clays of Cretaceous, Tertiary, and Quaternary age. These transgressive and regressive sequences of unconsolidated sediments vary in thickness from zero at the northern boundary with the New Jersey Piedmont, to greater than 6,000 feet in the vicinity of Cape May at the extreme southeastern tip of New Jersey. Locally at the site, the Coastal Plain sequence has been shown to be over 2,250 feet thick, typically striking northeast-southwest and dipping gently to the southeast. The Coastal Plain sediments that are of significance to this case study are those which occur within the upper 250 feet of the sequence. These include the Tertiary age sediments of the Kirkwood and Cohansey formations. These formations have been informally subdivided into seven hydrostratigraphic units consisting of four aquifers and three aquitards. The stratigraphic relationship and nomenclature of each unit are presented on Figure 2. The Primary Cohansey Aquifer is the regional water table aquifer and its water table surface is typically encountered beneath the site at depths ranging from 30-40 feet below ground surface.

The clay unit defined as the Cohansey Yellow Clay lies within the unsaturated zone in the western portion of the site and generally dips to the east where it intersects and dips below the Primary Cohansey Aquifer water table. The Yellow Clay is discontinuous beneath the site. Where present, it is usually encountered between 20 and 30 feet below ground surface. It typically ranges in thickness from less than one foot to ten feet, with a vertical hydraulic conductivity of approximately 5×10^{-8} cm/sec (1.4×10^{-4} ft/day). Locally, perched ground water occurs atop the Yellow Clay. The lateral extent and saturated thickness of the perched ground water are controlled by recharge from precipitation events and the geometry of the clay surface.

Potential NAPL Source Areas

The site consists of 12 potential contaminant source areas (generalized), as identified by USEPA under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). The potential source areas represent those areas that may contain, and potentially release, contaminants to the subsurface based on former site activities. These activities include the former manufacturing processes, material handling, and disposal practices. Since each of these areas was considered to be a potential contaminant source area, they were all included as potential NAPL source areas as well. These potential NAPL source areas possess varying degrees of NAPL likelihood. The potential NAPL source areas are illustrated on Figure 1, with the areas being labeled A through L.

Operational Definition of NAPL

The validity of the NAPL field screening calibration depended upon the availability of a reliable procedure for determining the presence or absence of NAPLs in a soil sample. This determination procedure had to provide a degree of confidence sufficient to reliably calibrate NAPL field screening results against it. No such proven procedure was readily available. Although some general guidelines were available, including some USEPA guidance (USEPA, 1992), these methods are generic and cannot readily accommodate site-specific conditions such as soil characteristics and NAPL composition.

Therefore, a site-specific “Operational Definition of NAPL” (ODN) was developed that could be used as an effective tool for determining the probable presence or absence of NAPLs in a soil sample by applying the ODN to soil sample analytical results. The ODN developed for the site was based on the method developed by Feenstra et al. (1991), which evaluates the potential for NAPLs in a soil sample based on the total organic compound concentrations in the soil sample and the partitioning of the compounds among the soil particles, pore water, and pore air space. Certain physical and chemical properties of the soil are used to estimate the maximum theoretical dissolved concentration of a particular compound within the pore water for either saturated or unsaturated soils. The pore water concentration of individual compounds detected in a given soil sample is calculated from the total sample concentration data. If the calculated pore water concentration exceeds the upper solubility limit for that compound, then residual NAPL is likely present in the sample. Feenstra et al.’s (1991) basic equations for the method are as follows:

Unsaturated Zone

$$C_w = \frac{C_t \rho_b}{(K_d \rho_b + \phi_w + H_c \phi_a)} \quad \text{Equation 1}$$

Saturated Zone

$$C_w = \frac{C_t \rho_b}{K_d \rho_b + \phi_w} \quad \text{Equation 2}$$

Where: C_w = chemical concentration of compound in pore water (parts per million, ppm)
 C_t = total soil concentration of compound (ppm)
 ρ_b = dry bulk density (g/cm³)
 ϕ_w = water-filled porosity (fraction of the porous medium volume)
 ϕ_a = air-filled porosity (fraction of the porous medium volume)
 H_c = Henry's Law Constant (dimensionless)
 K_d = partition coefficient between pore water and soil solids (cm³/g)
 $K_d = K_{oc} f_{oc}$
 K_{oc} = organic carbon-water partition coefficient (cm³/g)
 f_{oc} = fractional organic carbon in soil

Equations 1 and 2 can be rearranged, and based on the effective solubilities of the NAPL constituents, a "threshold concentration" for each potential NAPL constituent in soil is calculated. The presence of NAPLs is likely for samples in which one or more of the constituents are detected above their calculated NAPL threshold concentrations. The equations for calculating the threshold concentrations for unsaturated zone and saturated zone soil samples are as follows:

Unsaturated Zone

$$C_{\text{threshold}}^i = \left[\frac{K_d^i \rho_b + \phi_w + H_c \phi_a}{\rho_b} \right] S^i X^i \quad \text{Equation 3}$$

Saturated Zone

$$C_{\text{threshold}}^i = \left[\frac{K_d^i \rho_b + \phi_w}{\rho_b} \right] S^i X^i \quad \text{Equation 4}$$

Where: $C_{\text{threshold}}^i$ = soil threshold concentration for compound i
 K_d^i = soil/water distribution coefficient of sorption for compound i
 ρ_b = dry bulk density
 ϕ_w = water-filled porosity
 ϕ_a = air-filled porosity
 H_c = dimensionless Henry's Law Constant
 S^i = pure-phase upper solubility limit of compound i
 X^i = mole fraction of compound i in the NAPL

The calculated site-specific NAPL threshold concentrations for 20 compounds are shown on Table 1. Those 20 compounds were considered to be the likely NAPL constituents at the site since they were most prevalent in soil and groundwater samples collected from the site in the past. Table 1 also presents other compound-specific parameters used to calculate the threshold concentrations. The threshold concentrations given are for unsaturated soil samples. Saturated soil threshold concentrations are slightly higher.

Development of the ODN then used the rearranged Feenstra et al.'s (1991) equations to calculate a dimensionless ratio termed the "Threshold Ratio Summation", or TRS value (Page, et al., 1996), which was used as an indicator of the probable presence or absence of NAPL in a given soil sample. The TRS value incorporates both the measured concentration for each NAPL compound in a given soil sample and a site-specific upper threshold concentration calculated for each of those compounds. This method does not require direct determination of mole fractions of a compound in a sample. The following is the derivation of the ODN, namely the TRS value (the unsaturated zone example is presented here, but the derivation process is identical using the saturated zone example):

$$C_{\text{threshold}}^i = \left[\frac{K_d^i \rho_b + \phi_w + H_c \phi_a}{\rho_b} \right] S^i X^i \quad \text{Equation 3}$$

$$C_{\text{upper threshold}}^i = \left[\frac{K_d^i \rho_b + \phi_w + H_c \phi_a}{\rho_b} \right] S^i \quad \text{Equation 5}$$

Where: $C_{\text{threshold}}^i$ = soil threshold concentration for compound i (assumes multi-constituent NAPL)
 K_d^i = soil/water distribution coefficient of sorption for compound i
 ρ_b = dry bulk density
 ϕ_w = water-filled porosity
 ϕ_a = air-filled porosity
 H_c = dimensionless Henry's Law Constant
 S^i = pure-phase upper solubility limit of compound i
 X^i = mole fraction of compound i in the NAPL

$C_{\text{upper threshold}}^i$ = threshold concentration for compound i based on upper solubility limit
(assumes single constituent NAPL)

Solving for X^i :

$$\frac{C_{\text{threshold}}^i}{C_{\text{upper threshold}}^i} = X^i \quad \text{Equation 6}$$

If all compounds are present at their threshold concentration, and all major components are considered:

$$\sum_i \frac{C_{\text{threshold}}^i}{C_{\text{upper threshold}}^i} = \sum_i X^i = 1$$

In a sample containing NAPL:

$$C_{\text{measured}}^i > C_{\text{threshold}}^i$$

In a sample containing much NAPL:

$$C_{\text{measured}}^i \gg C_{\text{threshold}}^i$$

Therefore, if NAPL is present:

$$\sum_i \frac{C_{\text{measured}}^i}{C_{\text{upper threshold}}^i} > \sum_i \frac{C_{\text{threshold}}^i}{C_{\text{upper threshold}}^i} = 1$$

Since $\sum_i \frac{C_{\text{measured}}^i}{C_{\text{upper threshold}}^i}$ is the TRS value, then if NAPL is present in a sample:

$$\text{TRS} > 1$$

If NAPL is present in a given soil sample, the TRS value should be greater than 1.0. This assumes the ideal case that all major NAPL constituents are identified and their concentrations are accounted for in the calculation. In practical application, it is not likely that all NAPL constituents will have been included in the evaluation, as there will always be an unidentified portion. Therefore, in practical application it is possible to calculate TRS values less than 1.0 even for a sample containing residual NAPLs.

During a separate case study of soil analytical data from Area H at the site, it was determined that a sample yielding a TRS value as small as 0.1 could be indicative of residual NAPLs. For this reason, samples yielding TRS values of 0.1 to 1.0 were considered to warrant closer examination in order to determine whether NAPL is likely present. This premise was employed for the NAPL field screening calibration.

Using the ODN described above, TRS values were calculated for each of the soil analytical sample results included in the field calibration. Depending on whether the sample was collected from the saturated or

unsaturated zone, the appropriate upper threshold value was used. The calibration process consisted of comparing the results of each of the field screening methods to the corresponding TRS value to assess whether the field screening results agree with the TRS value with respect to the likely presence or absence of NAPLs.

Bench-Scale Studies

The purpose of the bench-scale studies was to evaluate the applicability of the proposed NAPL field screening methods to specific compounds that have been routinely detected in soil and groundwater samples from the site. The bench-scale evaluation was conducted to provide a qualitative evaluation of the field screening methods. A more detailed quantitative evaluation was performed during the field calibration phase. Specific objectives of the bench-scale evaluation included the following:

- To evaluate the ability of each of the proposed methods to identify the NAPL compounds likely to be present at the site.
- To evaluate the relative sensitivity of the proposed methods with respect to NAPL content.
- To evaluate the repeatability of results obtained by the different screening methods.
- To establish a hierarchy of the screening methods based on reliability and sensitivity.
- To optimize the sample handling and screening procedures to maximize the ability to identify NAPLs.

Other investigators have conducted similar types of studies. Namely, Cohen, et al. (1992) performed bench-scale experiments to evaluate various visual means for detecting NAPLs in soil. The bench-scale studies discussed here were generally patterned after their work.

The following four compounds (of the 20 listed in Table 1) were selected for study because they are commonly detected in soil and groundwater at the site in significant concentrations, and therefore would be likely constituents of any residual NAPL that may be associated with the site: trichloroethene (TCE), 1,2-dichlorobenzene (DCB), chlorobenzene, and 1,2,4-trichlorobenzene (TCB). A one-liter bottle of high-grade chemical (approximately 99 percent purity) was obtained for each of these compounds. In addition to these four individual NAPL compounds, a mixture was also prepared consisting of equal volumes of each of these four NAPL compounds. These four individual NAPL compounds and one compound mixture were the focus of the study.

Representative site soil was used as the matrix for the bench-scale evaluation. Review of grain-size distribution curves for site sands and fractional organic carbon content data supported the physical description of the soils that indicate that the site soils are relatively homogeneous with little variation from different areas of the site. The soil used in the bench-scale evaluation was obtained from a "background" area of the site, away from potential sources of contamination. The soil was dried in an oven at 100°C for approximately 90 minutes to remove any residual soil moisture. Approximately 185.5 grams (70 cm³, assuming a soil particle density of 2.65 g/cm³) of soil was weighed and placed into each container.

Each sample set consisted of three containers, including two 8-ounce glass containers and one 8-ounce polyethylene container. The polyethylene container was used for the hydrophobic dye shake test because NAPLs generally will wet plastic better than glass (Cohen et al., 1992). One of the glass containers was used for the head-space analysis, and a small piece of aluminum foil was placed over its opening before securing the lid. The second glass container was used for visual observations and the UV fluorescence scanning.

An aliquot (0.1 mL, 1.0 mL, and 10 mL) of each NAPL compound and the NAPL mixture was added to each designated soil sample container set using dedicated pipettes. These spike aliquots yielded approximate NAPL residual saturations (equal to the volume of NAPL divided by total porosity of the soil) ranging from 0.33 to 33.3 percent (i.e., portion of pore space occupied by residual NAPL). Therefore, the bench-scale study evaluated residual NAPL saturations well below the typical residual NAPL range of 10 to 50 percent (Cohen et al., 1992). Using unsaturated soil samples completely void of moisture allowed an evaluation of the effects of soil moisture on the field screening methods by using the extreme values of expected moisture content (i.e., 0% to 30% by volume). For the saturated sample sets, tap water was added to each container to bring the total liquid volume, including any NAPL, to approximately 30 mL (or 30 percent). This volume was chosen to simulate the estimated total porosity (30 percent) of the site soil.

In order to further test the sensitivity of the field screening methods, aliquots of 0.05 mL and 0.01 mL of the NAPL mixture were added via syringe to separate sample container sets for both saturated and unsaturated samples. The corresponding NAPL residual saturations for these samples were approximately 0.17 percent and 0.03 percent, respectively.

The sample sets were labeled such that the examiners did not know the sample NAPL concentration or whether the sample contained NAPL. A total of 34 spiked soil sample sets (17 saturated and 17 unsaturated) plus six blank (no NAPL added) sample sets (three saturated and three unsaturated) were prepared for evaluation, for a grand total of 40 sample sets tested. Two examiners were used in the bench-scale studies to evaluate repeatability of applying the field screening methods.

Testing Procedures

Visual Observation:

Each sample was visually examined for evidence of NAPLs. Since the NAPL compounds used in this study were clear and colorless, the examiners primarily looked for phase-separated liquids.

Hydrophobic Dye Shake Test:

Under a Class A fume hood, approximately 1 mg of Sudan IV was added to the appropriate plastic sample container. Tap water was then added to the sample until the water level was above the surface of the soil; then the container was manually shaken for approximately 10 seconds. The container was then visually inspected for red-dyed NAPL.

UV Fluorescence:

A hand-held Raytech Industries UV lamp Model R5-FLS was used to scan the soil samples. The lamp emits both short-wave UV and long-wave UV simultaneously. Samples were examined by emptying the

soil sample onto a paper plate and scanning the sample with UV light in a dark room. The sample was manipulated with a metal spatula during the scanning in order to expose soil surfaces.

Head-Space Analysis:

An HNu Systems photoionization detector (HNu) equipped with a 11.7 eV lamp, and a Foxboro Organic Vapor Analyzer (OVA) equipped with a flame ionization detector were used to measure total organic vapors in the sample jar head-space. Before conducting the head-space analyses, the HNu and OVA were calibrated in accordance with the manufacturer's calibration procedures. The HNu was calibrated to isobutylene and the OVA was calibrated to methane.

The sample containers for the head-space analyses were allowed to equilibrate to room temperature. Each jar was shaken for approximately 30 seconds prior to removing the lid to expose the aluminum foil. The foil was pierced with the tip of the HNu and the measured concentration was recorded. Next, the OVA was used to measure vapors in survey mode (in this mode the OVA measures total organic vapors present), and the measurement was recorded. The foil was then discarded and the screw-on lid was replaced on the container.

A detailed discussion of the results of the bench-scale studies is beyond the scope of this article. However, the principle conclusions of the studies are presented in the following section.

Conclusions of Bench-Scale Studies

The results of the bench-scale evaluation suggest the following conclusions:

- The hydrophobic dye shake test and head-space analysis using an HNu were the most effective methods for identifying the presence of NAPL compounds tested. The head-space analysis results support the NAPL "cut-off" concentration discussed in the NAPL Action Plan and head-space analysis can indicate the presence of residual NAPL with a high degree of confidence. In the bench-scale evaluation using a combination of these two methods, the presence of NAPL in the samples was correctly identified over 90 percent of the time. [A threshold value of 100 parts per million vapor (ppm_v) for head-space HNu readings was used since this was established as a reasonable cut-off concentration above which residual NAPL is likely to be present, based on the method developed by Feenstra, et al. (1991) (Watkins, et al. 1995).]
- No NAPL could be identified through unaided visual observations. However, this method still might be effective in the field in areas where colored NAPL may be present.
- UV fluorescence proved ineffective for the determination of the NAPL compounds tested due to their lack of visually detectable fluorescence. However, this method may be of greater use in the field where NAPL compounds fluorescing in the unaided visible range might be present or where visually fluorescent impurities might be present in the NAPLs.
- The proposed field methodologies can be used by different examiners with repeatable results.

- Extreme care should be exercised during sample handling to optimize the effectiveness of the screening methods and minimize potential for volatile losses or cross-contamination among samples.

Field Calibration

This section evaluates the NAPL field screening methods with respect to their sensitivity and applicability at the study site as determined during the field calibration. In theory, the calibration process would compare calculated TRS values to a NAPL "threshold" TRS value to determine the presence or absence of NAPL in a soil sample. However, as discussed previously, an earlier case study applying the TRS method to soil data from Area H of the study site concluded that a TRS value greater than 0.1 but less than 1.0 (i.e., $0.1 < \text{TRS} < 1.0$) could be indicative of residual NAPLs. TRS values greater than 1.0 are considered indicative of the presence of residual NAPL with a high degree of confidence. Therefore, TRS values between 0.1 and 1.0 define an uncertainty range within which data do not conclusively indicate the presence or absence of NAPLs. For this evaluation, NAPL field screening results have been compared, or calibrated, to the TRS values of 0.1 and 1.0.

In order to calibrate the NAPL field screening methodologies, it was important to obtain and evaluate both soil samples with NAPLs and soil samples without NAPLs. To meet this goal, two areas at the site were chosen that had a high potential for NAPLs to be present based on previous investigations and site history. These were subareas of Area A and Area F. These subareas were termed Area A1 and Area F1. Area F1 included a former underground storage tank (UST) area. A total of 77 soil samples collected from these two areas were used for the field calibration. The field calibration process for the Areas A1 and F1 soil samples consisted of comparing the results of each of the field screening methods to the corresponding TRS value calculated from the CLP analytical data to assess whether the screening results agreed with the calculated TRS value with respect to indicating the presence or absence of residual NAPL. The results of the field calibration are illustrated in Table 2 and summarized below.

Visual Observation:

No NAPL was conclusively identified through visual observation during field calibration. Field descriptions included a variety of visual observations of soil samples, later identified as containing NAPLs (via TRS values), such as colorless liquid with a strong odor, liquid with sheen, and purple sand with strong odor. Strong sample odor was a more obvious and consistent indicator of the probable presence of NAPLs, although odor alone was not conclusive. When used alone, visual identification of NAPLs in soil samples collected at the study site proved difficult and unreliable at best. No colored NAPL was identified during the field calibration. "Stained" soils were not necessarily indicative of NAPLs, and visually "clean" soils occasionally contained NAPLs.

Field Head-Space Measurement:

The highest TRS value corresponding to a head-space measurement indicating absence of NAPLs (i.e., less than 100 ppm_v) was 0.12 (greater than 0.1 but less than 1.0). This suggests that head-space measurement is very sensitive to possible NAPL compounds in the soil. In fact, head-space results yielded a very low rate of false negative results (i.e., when head-space indicated no NAPLs present, but the corresponding TRS value indicated NAPLs). False negative results occurred for head-space analysis at a rate of seven

percent relative to a TRS value of 0.1. No false negatives results occurred relative to a TRS value of 1.0. This suggests that comparing head-space results relative to either a TRS value of 0.1 or 1.0 is a viable means of determining the likely presence or absence of NAPLs.

The lowest TRS value corresponding to a positive head-space measurement (i.e., greater than 100 ppm_v) result was <0.01. This suggests that head-space analysis of samples was more likely to indicate false positive results. NAPL head-space measurements yielded false positive results at a rate of 16 percent relative to a TRS value of 0.1, and at 21 percent relative to a TRS value of 1.0. High head-space concentrations would occur in samples containing high soil vapor concentrations produced by highly volatile compounds. Fugitive soil vapors from the highly volatile NAPL compounds (e.g., trichloroethene and tetrachloroethene) present in namely Area F1 soils produced anomalously high head-space measurements, resulting in false-positive NAPL indications. Although some false positives were observed, this method was not likely to miss detection of NAPLs actually present.

Hydrophobic Dye Shake Test:

The lowest TRS value corresponding to a positive hydrophobic dye result was 1.8. This value suggests that the dye test method is only sensitive enough to detect NAPL-impacted soil at the study site with a TRS value equal to or greater than approximately 1.8. There were no cases of dyed samples with a calculated TRS value less than 0.1 (i.e., there were no false positive dye test results). There were cases, however, where a sample was not dyed but the corresponding TRS value was greater than 0.1 (i.e., the dye reported a false negative result). The rate of dye test false negatives relative to a TRS value of 0.1 was 40 percent ; versus a 10 percent false positive rate relative to a TRS value of 1.0. False negative results may be caused by samples with minimal or subtle red dyeing not observed by the examiner. Cohesive clay or silt matrices could also inhibit the even distribution of dye throughout the sample thereby preventing contact between dye and potential NAPLs in the clay or silt pore space. Eliminating clay samples from the test group yielded false negative rates of 20 percent and 0 percent relative to TRS values of 0.1 and 1.0, respectively.

Matrix grain size and color can also limit the effectiveness of hydrophobic dye. As discussed above, cohesive matrices can prevent the complete distribution of dye throughout the sample. Red or dark-colored soil matrices can mask the red Sudan IV dye color. Only a limited surface area of sample is visible at any one time for visual examination through the sample container. Thus, isolated globules of NAPLs hidden from the observer may not be consistently identified.

Hydrophobic dye testing with Sudan IV proved to be effective for identification of NAPL-impacted soils collected during the field calibration. The reliability of the method was improved if results were considered in conjunction with other field screening methods (e.g., the head-space screening method).

Ultraviolet Fluorescence (UV):

Review of the analytical data from the soil samples collected indicated that distinctly different NAPLs comprised of different compounds are present in each of the two areas investigated. The Area A1 NAPLs apparently are comprised of predominantly petroleum hydrocarbons (e.g., toluene, xylenes, etc.). The Area F1 NAPLs apparently are comprised mostly of chlorinated organic compounds (TCE, PCE, chlorobenzene, dichlorobenzenes, etc.). Given that these different classes of compounds have different fluorescent properties, they were evaluated separately.

The only two soil samples collected from Area A1 that exhibited fluorescence attributable to NAPLs were collected from the former UST Area. The lowest TRS value corresponding to a positive UV test result was less than 0.1. This suggests that UV testing is sensitive to the NAPL compounds present in the UST Area, although the data set is quite small.

Although TRS values for several Area F1 samples indicated the presence of NAPLs, no samples exhibited fluorescence attributable to NAPLs. Therefore, UV testing is not considered a sensitive or reliable method for identifying the type of NAPLs contained in Area F1.

As determined from the bench-scale studies, the UV method is limited to fluorescence visible to the unaided eye. Therefore, to be used effectively as a NAPL screening method, the NAPLs must fluoresce within the unaided visible range. This makes UV testing a useful screening method for hydrocarbon-based NAPLs such as was encountered in Area A1 but eliminates it as an indicator of the chlorinated compounds encountered in Area F1.

Because no fluorescence due to residual NAPLs was observed in NAPL-impacted samples from Area F1, the UV method does not seem applicable for identifying NAPLs comprised of chlorinated solvents such as those identified in the Area F1 subsurface soils. However, the UV screening method does seem promising for identifying petroleum-based NAPLs such as those identified in Area A1. This is consistent with the historical use of UV as an accepted screening method for identifying the presence of petroleum in potential reservoir rock during oil exploration.

Summary

The NAPL field screening methodology results were compared and calibrated to the corresponding soil analytical results. All field screening method results were compared to the calculated TRS values. For the purposes of calibrating the field screening methods, a TRS NAPL "threshold" value of 0.1 and 1.0 were individually evaluated, realizing that the actual NAPL threshold value would probably be somewhere between those two values. The rates of false positives and false negatives were evaluated for each of the screening methods. A false positive was when a field screening method suggested the presence of NAPLs but the corresponding TRS value was below the given NAPL "threshold" value. A false negative was when a field screening method did not detect any NAPL but the corresponding TRS value was above the given NAPL "threshold" value.

Head-space measurement by HNu combined with hydrophobic dye shake testing proved to be the most sensitive and reliable field screening methods, displaying a high degree of accuracy when used together for identifying the presence of NAPLs in soil samples from Areas A1 and F1. A combination of these methods proved to be a very effective screening procedure for rapidly and reliably determining the presence or absence of residual NAPLs in soil at the study site.

Ultraviolet fluorescence (UV) testing and visual observation methods were not reliable NAPL field screening methods for the site soils evaluated. UV testing was effective for identification of petroleum hydrocarbon-based NAPLs encountered in Area A1. However, UV testing was ineffective for detecting chlorinated solvent-based NAPLs encountered in Area F1. No NAPLs could be definitively identified by unaided visual examination of soil samples collected from either area since no colored NAPLs were identified during the investigation, and "stained" soils were not necessarily indicative of the presence of NAPLs. However, these methods could still prove useful if different types of NAPLs (e.g., colored, or

fluorescent in the unaided visible range) were encountered in the future at the site. The UV fluorescence might also be useful in differentiating significantly different NAPL types (i.e., petroleum hydrocarbon-based versus chlorinated solvent-based) in the field.

The calibrated NAPL field screening methods were incorporated into the ongoing NAPL investigation at the site as the primary means of determining the presence or absence of NAPLs in soil samples. These methods, coupled with only periodic analytical samples for confirmation and calibration checks offer an effective tool for a dynamic field investigation designed to be modified in the field and tailored to the results of the data being collected. The methodology employed in the NAPL investigation has been approved and supported by the USEPA. The use of calibrated NAPL field screening methods is a cost-effective alternative to the collection of vast amounts of soil quality data and the calibration process described in this article likely has direct relevance and applicability to other sites faced with performing detailed NAPL investigations.

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TABLE 1: PROPERTIES OF POTENTIAL NAPL COMPOUNDS

Compound	Henry's Law Constant (dimensionless)	Solubility Limit ($\mu\text{g/l}$)	K_{oc} (ml/g)	K_d (ml/g)	Threshold Concentration ($\mu\text{g/kg}$)
Anthracene	2.71E-03	75	66,830	86.9	6,520
Benzene	2.28E-01	1,780,000	186	0.241	573,722
Chlorobenzene	1.87E-01	490,000	178	0.231	150,743
2-Chloronaphthalene	2.55E-02	6,740	5,604	7.29	49,498
2-Chlorotoluene	2.60E-01	72,000	553	0.719	57,815
4-Chlorotoluene	7.08E-01	44,000	727	0.945	47,498
1,2-Dichlorobenzene	4.99E-02	100,000	500	0.650	71,147
1,3-Dichlorobenzene	1.96E-01	69,000	615	0.800	60,511
1,4-Dichlorobenzene	1.87E-01	80,000	566	0.736	65,024
Ethylbenzene	2.75E-01	152,000	828	1.076	176,612
Naphthalene	1.91E-02	31,000	2,162	2.81	88,919
Nitrobenzene	1.02E-03	1,900,000	229	0.298	671,865
Phenanthrene	1.07E-03	1,180	15,090	19.6	23,214
1,1,2,2-Tetrachloroethane	1.90E-02	2,900,000	83	0.107	478,446
Tetrachlorethene	6.37E-01	150,000	427	0.555	102,181
Toluene	2.79E-01	515,000	155	0.201	148,201
1,2,4-Trichlorobenzene	9.57E-02	19,000	3,398	4.42	85,176
Trichloroethene	3.79E-01	1,000,000	130	0.169	267,067
1,2,3-Trichloropropane	1.32E-02	1,750,000	102	0.132	331,275
Xylenes, total	2.93E-01	189,000	293	0.381	88,581

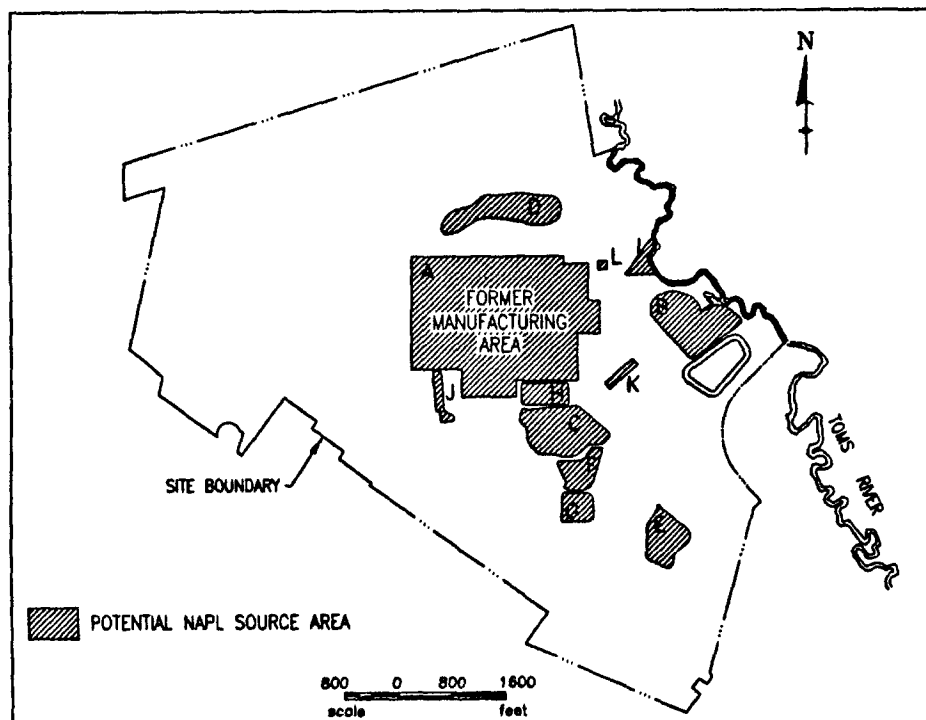


FIGURE 1: SITE PLAN SHOWING POTENTIAL NAPL SOURCE AREAS

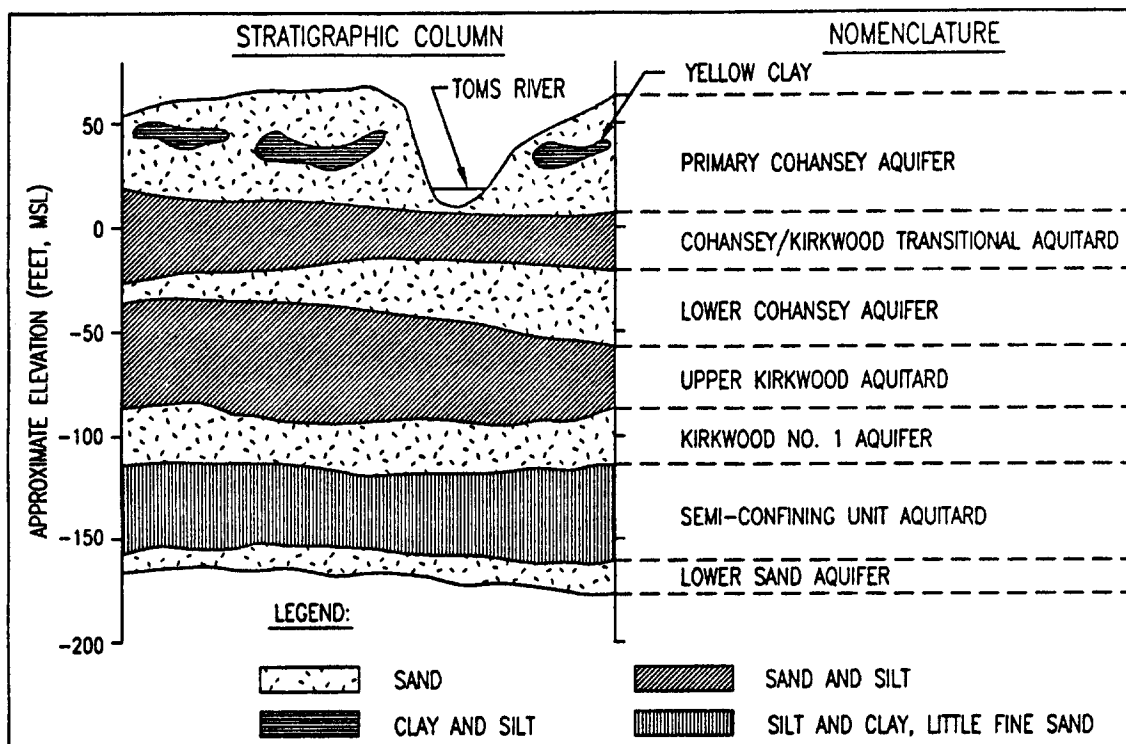


FIGURE 2: GENERALIZED SITE STRATIGRAPHY AND NOMENCLATURE

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